

Immobilization mechanism of Pb in fly ash-based geopolymer



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HIGHLIGHTS

- The behavior of Pb in geopolymer depends on the chemical property of the Pb compound.
- Pb participates in the formation of geopolymer network, forming leaded amorphous gel.
- Dissolution of lead compounds is a vital step in the formation of leaded geopolymer.
- Pb compounds, soluble in alkali, are chemically bonded into the geopolymer gel.
- PbS, inert to alkali, is trapped in the geopolymer by physical encapsulation.

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ABSTRACT

Geopolymer possesses good immobilization capacity for Pb. There are two rival interpretations regarding the immobilization mechanism of Pb. This research investigates the behavior of 3 Pb compounds in geopolymer and clarifies the immobilization mechanism. When Pb contamination is added in the form, soluble in sodium hydroxide solution, the Pb is converted to an amorphous form and participates in the formation of geopolymer network. Successful immobilization of these species relies on chemical bonding and physical encapsulation. On the contrary, the Pb compound inert to sodium hydroxide solution is segregated from the binder and trapped by physical encapsulation.

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1. Introduction

Geopolymer, the reaction product of a solid aluminosilicate with a highly concentrated aqueous alkali hydroxide or silicate solution [1], is a type of cementitious material with an amorphous or semi-crystalline nature [2]. Geopolymer can provide comparable strength performance to traditional binders in practical applications [1]. Due to its low permeability, long-term durability and resistance to acid attack [3], geopolymer is believed to be a good immobilization system for various hazardous waste. There have been an increasing number of studies that focus on the potential application of geopolymer to immobilize heavy metals during the last decade [4–9]. Research into this field have two main objectives [10], i.e. (a) the immobilization efficiency and mechanism should

be determined, and (b) the physical properties should be stable, not only to encapsulate toxic metals, but also to make the product suitable for further building applications.

A great many hazardous solid wastes are proved to be suitable as a source material for making good geopolymeric materials, such as municipal solid waste incineration fly ash [2], lead smelting slag [11], and primary lead slag [12]. The synthesized geopolymer possess a comparable compressive strength with Ordinary Portland Cement. In addition, most of the heavy metals that are presents in these wastes can be effectively immobilized in geopolymer. It is worth noting that these synthesized geopolymer possess good immobilization capacity for Pb.

The immobilization mechanism of heavy metals in geopolymer is always a popular research, especially of Pb [4,5,13–15]. There are two rival interpretations regarding the immobilization mechanism of Pb. One is that Pb is likely to be bonded into the amorphous geopolymer gel, which was proposed by van Jaarsveld et al. [4]. It means that the Pb is in an amorphous form. Perera et al. also concluded that Pb may be mainly in the amorphous aluminosilicate structure [13]. The other interpretation is that Pb is immobilized

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in the form of Pb_3SiO_5 , which is an insoluble crystalline compound [14]. Zhang et al. observed the Pb-rich regions in the SEM micrographs of the geopolymer with 0.5% Pb as $\text{Pb}(\text{NO}_3)_2$ [15]. The composition of the Pb-rich regions was approximately consistent with the Pb_3SiO_5 phase. He concluded that the effect of heavy metal immobilization in geopolymer depends on the form of the supplied contaminant. In sum, the difference between the two interpretations is the existing form of Pb bonded into geopolymer.

Thus, it is clear that more work is required to settle the controversy and find out the exact immobilization mechanism. In this paper, Pb compounds were used as the simulated lead-laden wastes to mix with aluminosilicate source for synthesis of geopolymer. Fly ash was used as the aluminosilicate source, because it is the most common source material for geopolymerization and its cost effectiveness [16]. This paper focused on the geopolymer containing three types of Pb compounds: PbO, PbSO_4 and PbS. These Pb compounds are chosen based on the following aspects:

1. PbO, PbSO_4 and PbS are three types of the primary Pb contaminants existing in the environment [17]. In soil, lead exists mainly as PbSO_4 and PbO [18]. In the atmosphere, lead is present mainly as PbSO_4 [19]. Lead particles emitted from mining and smelting processes are mainly in the form of PbSO_4 , PbO· PbSO_4 , and PbS [19,20].
2. Lead ion is amphoteric specie. This character of Pb has not been considered in the previous researches on the immobilization mechanism of Pb in geopolymer. The activators provide alkaline condition for the geopolymeric reaction. Many Pb compounds, such as PbO and PbSO_4 , can dissolve in excess alkali to form plumbite ions. Toxicity Characteristic Leaching Procedure (TCLP) [21] leaching test is often used to evaluate the immobilization efficiency. Acetic acid solution is used as extraction fluid in the TCLP test. Some Pb compounds can also react as a base and dissolve in acetic acid solution, such as PbO. The immobilization mechanism of Pb in geopolymer may be related to the chemistry property of Pb contamination. Thus, PbO, PbSO_4 and PbS were chose to simulate lead-laden wastes based on their solubility in acetic acid and alkali. Table 1 shows the solubility of these compounds.

In this paper, research was conducted to establish links between the immobilization mechanism of Pb and chemical properties of the supplied Pb compounds. The amounts of Pb added as different Pb compounds were 1%, 2%, 8% of fly ash weight. The purposes of this research were to (a) investigate the change of Pb before and after geopolymerization; (b) study the distribution of Pb in geopolymer; (c) assess the immobilization efficiency of different Pb compounds by geopolymer; (d) investigate the upper limit of the Pb content could be immobilized in the geopolymer.

Table 1
The solubility of the chosen Pb compounds.

Categories	Pb compounds	Solubility in acetic acid solution	Solubility in sodium hydroxide solution
1	PbO	Soluble	Soluble
2	PbSO_4	Unreactive	Soluble
3	PbS	Unreactive	Unreactive

Table 2
Chemical composition of the fly ash in terms of oxides.

Oxide	SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	K_2O	MgO	TiO_2	LOI
Mass%	52.1	23.5	7.6	9.3	0.9	1.9	0.9	1.1	0.5

LOI = loss on ignition at 1000 °C.

2. Experimental program

2.1. Materials

Fly ash, class F, according to the ASTM C618, was obtained from the Shenhua Power Station, Taicang, Jiangsu Province, China. The fly ash is of coal origin. The chemical composition, determined by X-ray fluorescence, is shown in Table 2. Analytical grade reagents PbO, PbSO_4 , PbS and NaOH were used. The silicate modulus (M_s) of the sodium silicate solution is 3.6. Distilled water was used throughout.

2.2. Synthesis

Fly ash and Pb compounds were mixed and ground in a ball mill for 30 min. NaOH, distilled water and sodium silicate solution were mixed and heated at 65 °C for 10 min. Then the mixed powder was added in the alkaline activator ($1.3\text{SiO}_2\cdot\text{Na}_2\text{O}\cdot 14.4\text{H}_2\text{O}$), followed by further 5 min mixing. Table 3 shows the summary of the matrices under discussion. The mass ratio of activator to solid material and the composition of the activator were chose based on previous work in which the geopolymer prepared from same fly ash and activator showed the optimal strength. The pastes were cast in steel $20 \times 20 \times 20$ mm cubic molds for the strength test and in $\phi 8.5 \text{ mm} \times 4 \text{ mm}$ plastic cylindrical molds for the leaching test. All the samples were cured in an airtight container at 85 °C for 24 h. After that the samples were sealed in plastic bags for curing at room temperature, until other tests were carried out after 7 days of ageing. The mole ratios of Si/Al of the designed geopolymer are also showed in Table 3, which could be calculated as follows,

$$\text{Si/Al}_{\text{Mole}} = \frac{\frac{W_{\text{SiO}_2}}{100} \times (100 - W_{\text{Pb}}) + 100 \times R_{\text{A/S}} \times \frac{1.3 \times M_{\text{SiO}_2}}{1.3 \times M_{\text{SiO}_2} + M_{\text{Na}_2\text{O}} + 14.4 \times M_{\text{H}_2\text{O}}}}{\frac{W_{\text{Al}_2\text{O}_3}}{100} \times (100 - W_{\text{Pb}})} \times \frac{M_{\text{Al}_2\text{O}_3}}{2 \times M_{\text{SiO}_2}} \quad (1)$$

where W_{SiO_2} is the SiO_2 content in the fly ash (%); $W_{\text{Al}_2\text{O}_3}$ is the Al_2O_3 content in the fly ash (%); W_{Pb} is the amount of Pb compound added into the fly ash (%); $R_{\text{A/S}}$ is the ratio of activator (g) to solid material (g); M_{SiO_2} is the molar mass of SiO_2 ($\text{g}\cdot\text{mol}^{-1}$); $M_{\text{Na}_2\text{O}}$ is the molar mass of Na_2O ($\text{g}\cdot\text{mol}^{-1}$); $M_{\text{H}_2\text{O}}$ is the molar mass of H_2O ($\text{g}\cdot\text{mol}^{-1}$).

2.3. Samples analysis

The compressive strength tests were conducted after 7 days of ageing. Three samples were tested for each mechanical test. X-ray powder diffraction data was obtained using Rigaku Ultima IV X-ray diffractometer with Cu K α radiation, 40 kV voltage and 40 mA current at 20°/min scanning rate, from 5° to 60° 2 θ range. Microstructural studies utilized SEM (JSM-6510A, Japan) equipped with the energy dispersive spectra (EDS) analyzer. Backscattered electron images and microanalysis studies utilized polished samples and the ground powder. All the samples was coated with carbon before imaging. Energy dispersive spectroscopy (EDS) was used to measure Si, Al, S, and Pb signals. X-ray Photoelectron Spec-

Table 3
Matrix composition.

ID	Contaminant in solid components/wt.%	Solid components/wt.%	Activator/mole ratio	Activator/Solid material ratio /by mass	Si/Al mole ratios of the designed geopolymer samples
A	–	100% fly ash	1.3SiO ₂ ·Na ₂ O·14.4H ₂ O	0.55	2.27
B1	1% Pb as PbO	1.1% PbO + 98.9% fly ash	1.3SiO ₂ ·Na ₂ O·14.4H ₂ O	0.55	2.27
B2	4% Pb as PbO	4.3% PbO + 95.7% fly ash	1.3SiO ₂ ·Na ₂ O·14.4H ₂ O	0.55	2.29
B3	8% Pb as PbO	8.6% PbO + 91.4% fly ash	1.3SiO ₂ ·Na ₂ O·14.4H ₂ O	0.55	2.31
C1	1% Pb as PbSO ₄	1.5% PbSO ₄ + 98.5% fly ash	1.3SiO ₂ ·Na ₂ O·14.4H ₂ O	0.55	2.28
C2	4% Pb as PbSO ₄	5.9% PbSO ₄ + 94.1% fly ash	1.3SiO ₂ ·Na ₂ O·14.4H ₂ O	0.55	2.29
C3	8% Pb as PbSO ₄	11.8% PbSO ₄ + 88.2% fly ash	1.3SiO ₂ ·Na ₂ O·14.4H ₂ O	0.55	2.32
D1	1% Pb as PbS	1.2% PbS + 98.8% fly ash	1.3SiO ₂ ·Na ₂ O·14.4H ₂ O	0.55	2.27
D2	4% Pb as PbS	4.6% PbS + 95.4% fly ash	1.3SiO ₂ ·Na ₂ O·14.4H ₂ O	0.55	2.29
D3	8% Pb as PbS	9.3% PbS + 90.7% fly ash	1.3SiO ₂ ·Na ₂ O·14.4H ₂ O	0.55	2.31

troscopy (XPS) studies were carried out using a AXIS Ultra^{PLD} XPS system (Kratos Analytical Ltd., Japan). Binding energies were corrected with respect to the C 1s peak at 284.2 eV.

Leaching test was conducted to assess the immobilization efficiency following the United States Environment Protection Agency (US EPA) TCLP method No. 1311 [21]. According to the determination test of TCLP for the appropriate extraction fluid, an acetic acid solution with 2.88 ± 0.05 pH (fluid No. 2) and a liquid/solid ratio of $20 \text{ mL} \cdot \text{g}^{-1}$ was used. The samples were agitated in a horizontal agitation apparatus for 18 h and then filtered. The concentration of lead ions in the leachate was measured by the use of an Inductively Coupled Plasma Optical Emission Spectrometer (Thermo Fisher Scientific iCAP 6300, USA).

3. Results and discussion

3.1. X-ray diffractometry

The XRD diffractograms of some selected samples are shown in Fig. 1. Quartz and mullite are detected in all these samples. These are attributed to the stable phases from the fly ash. The XRD patterns of samples B3 and C3 exhibit similar features. No distinct Pb-containing compounds are detected in samples B3 and C3, although the additives are detected in their raw materials. However, PbS is detected in sample D3 and its raw materials. PbS is inert to alkali. It appears that the PbS remains intact throughout geopolymerization. On the contrary, PbO and PbSO₄, which are soluble in alkali, are converted to an amorphous form during geopolymerization. It can be assumed that the dissolving of Pb compounds is a critical step in this form transition. The right figure in Fig. 1

shows a large version of the area marked in dashed box. The usual ‘geopolymer hump’ [15] centered at $\sim 28\text{--}30^\circ 2\theta$ is observed in samples B3, C3 and D3. It is worth noting that Na₂SO₄ is detected in sample C3. It means that PbSO₄ was dissolved during geopolymerization. Then the SO₄²⁻ combined with the Na⁺ and separated from the activator.

3.2. Scanning electron microscopy

Fig. 2 shows the backscattered electron (BSE) images of the B3-r, C3-r and D3-r (the solid raw materials of samples B3, C3 and D3). The micrographs show that most of the fly ash particles hold their shape after grinding. The Pb compounds could be observed clearly.

Fig. 3 shows the BSE images of the polished samples A, B3, C3 and D3. The table in Fig. 3 shows the composition of the marked spots. BSE images are useful to detect contrast between the areas with different chemical composition. Due to the difference of chemical composition and shape between un-reacted particles and amorphous gel, it is easy to differentiate the un-reacted particles from the amorphous gel around them. It is noteworthy that PbS is observed in sample D3. However, there are no isolated Pb compounds in samples B3 and C3.

The composition of some un-reacted spherical fly ash particles was investigated by X-ray spot analysis. The mole ratio of Si/Al of the un-reacted particles ranges from 1.02 to 2.25, which is approaching that of the fly ash. The right table in Fig. 3 shows that the mole ratio of Si/Al of the geopolymer gel ranges from 3.71 to 4.24. The left table in Fig. 3 shows the mole ratio of Si/Al of the designed geopolymer. It is noteworthy that the Si/Al mole ratios of the geopolymer gel are higher than the Si/Al mole ratio of the

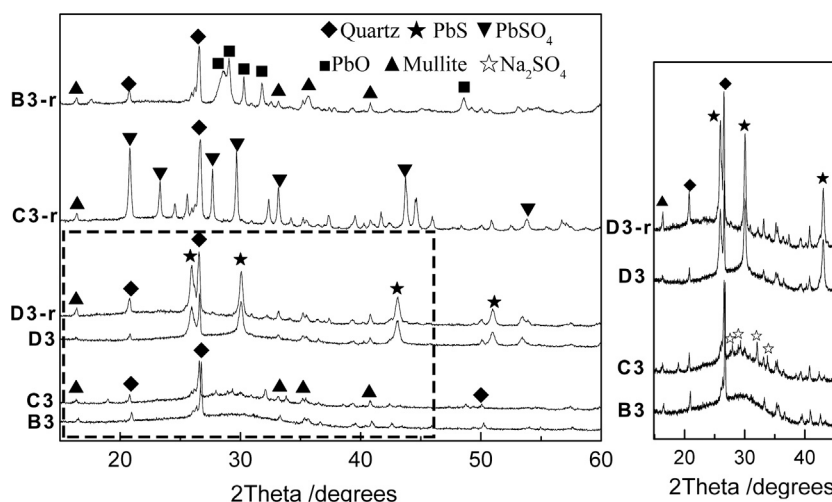


Fig. 1. The XRD diffractograms of the selected samples. The letter ‘r’ behind the sample ID represents the solid raw material of the matrices.

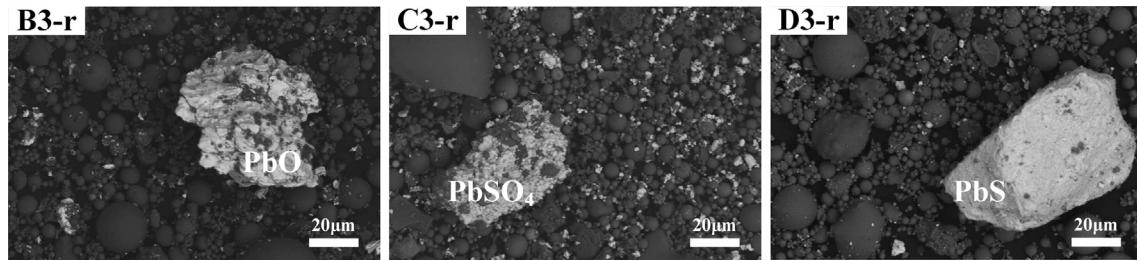
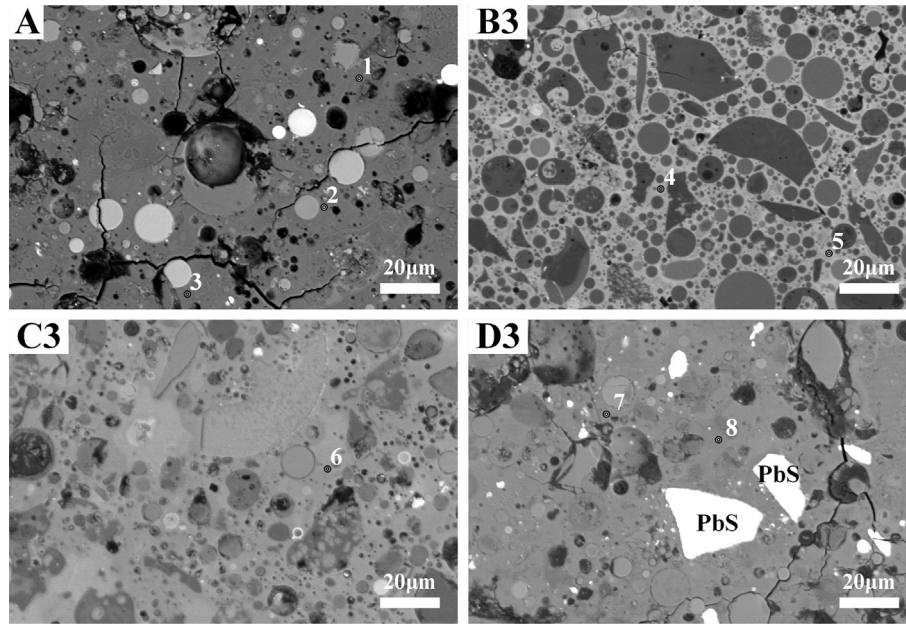


Fig. 2. The backscattered scanning electron images of the B3-r, C3-r and D3-r (the solid raw materials of samples B3, C3 and D3).



ID	Si/Al mole ratio of the designed geopolymer	Element Mass%	Element				Si/Al	
			Si	Al	Pb	S	Mass	Mole
A	2.27	A 1	29.52	7.32	-	-	4.03	3.87
		A 2	25.64	6.27	-	-	4.09	3.93
		A 3	29.73	7.19	-	-	4.13	3.97
B3	2.31	B3 4	21.96	4.98	22.34	-	4.41	4.24
		B3 5	23.71	7.42	15.56	-	3.20	3.07
C3	2.32	C3 6	17.90	4.06	9.36	3.17	4.41	4.24
D3	2.31	D3 7	22.68	5.88	2.73	0.89	3.86	3.71
		D3 8	28.65	7.03	1.89	0.39	4.08	3.92

Fig. 3. The backscattered scanning electron images of polished samples A, B3, C3, and D3.

designed geopolymer. Similar phenomenon was also found by Nikolić et al. [38] and Sindhunata et al. [22]. This phenomenon is frequently found in the geopolymer prepared from fly ash and high silicate concentration activator. The reasons lie in two aspects. (a) Only some parts of the fly ash participate in the geopolymeric reactions. The Si in geopolymer gel comes from the dissolved fly ash and the activator. The Al in geopolymer gel only comes from the dissolved fly ash. (b) The release rates of silicon and aluminum from fly ash are different [22]. During geopolymeric reactions, an excess of soluble silica was provided by the activator. In such conditions, a Si-rich gel is formed immediately [23]. Therefore, the Si/Al mole ratio of the geopolymer gel is higher than the Si/Al mole ratio of the designed geopolymer.

The major difference between samples A, B3, C3 and D3 is the grey level of the geopolymer gel. The grey level in the BSE image of a polished sample depends on the electron density of the analyzed sample volume, which is mainly related to the chemical compositions of the samples. The grey level of the gel phase of samples A and D3 is higher than that of the un-reacted fly ash. However, the opposite is the case for samples B3 and C3. It is noteworthy that Pb is clearly detected in the tagged spots 4, 5, 6. It seems that the Pb ions are converted to an amorphous form and distributed uniformly in the binder phase of samples B3, and C3. Combined with the X-ray diffractometry analysis, it can be expected that these Pb ions are chemically bonded into the amorphous network of the geopolymeric matrix. One thing that the Pb compounds supplied

Table 4
Compressive strengths of geopolymers with addition of NaNO_3 and PbNO_3 [15].

ID	Contaminant in solid components/wt.%	Compressive strength/MPa			
		7 days	14 days	28 days	105 days
F3	–	41.9	62.2	60.0	70.9
F5	0.5% Pb as PbNO_3	33.5	49.8	57.5	69.5
F10	0.3% NO_3^- as NaNO_3	45.7	64.5	59.2	56.6

The NO_3^- content of F5 and F10 are the same.

in samples B3 and C3 have in common is that they are soluble in alkali. PbS is almost insoluble in alkali and remains in its initial form in geopolymeric matrix. Thus, the behaviors of Pb compound in geopolymer are closely related to its solubility in alkali.

Geopolymer is either crystalline or non-crystalline (amorphous) [24]. In geopolymer, the key network forming cations are Al^{3+} and Si^{4+} [25], similar to glasses. In both systems, the alkali cations, such as Na^+ , act as network modifiers. Therefore, the theory of network formation of glasses may be partially applied to the geopolymer system. The role played by the Pb in the leaded glasses has been investigated over a number of years [26–30]. PbO is not a glass-forming oxide by itself, but when incorporated in considerable quantities into other glass-forming oxide systems, such as SiO_2 , B_2O_3 , TeO_2 and P_2O_5 , it can form glass [31]. The structural role of PbO in the oxide glasses is special, since lead oxide is known to behave both as a modifier and a network former, depending on its content added into the glass [32]. It is often suggested that Pb acts as a traditional modifier at low lead content and becomes a glass former at high lead content [27,28]. As for geopolymer, Pb may play a similar role in the formation of this geopolymer network. Both systems have similar components and structure. Thus, it is reasonable to conclude that the Pb will be converted to an amorphous form and participate in the formation of the geopolymer network when the Pb contamination is in the form, soluble in sodium hydroxide solution.

3.3. Compressive strength

The 7 days compressive strength of the geopolymer samples synthesized with different lead contaminants is listed in Table 5. From the comparison of the compressive strengths, it can be seen that the addition of PbO increased compressive strength. Other Pb compounds degrade the strength by varying degrees.

The 7 days compressive strengths of the geopolymer matrices containing PbO is increased as the Pb contamination increases from 1% to 8%. Zhang et al. investigated the compressive strength of the geopolymer synthesized with addition of NaNO_3 and PbNO_3 [15]. Table 4 shows the compressive strength of the geopolymer. He found that Pb^{2+} having a positive effect on the strength of the binder. It is important to note that the amount of Pb added was low in his research. In the current study, the increase of compressive strength is more obvious due to more Pb added. Thus, it is reasonable to conclude that the geopolymer network is modified by the dissolved Pb ions. As a result, the compressive strength is improved.

PbS remains in its initial form in geopolymeric matrices. Thus the interfacial bonding strength between PbS and geopolymeric gel is low. The PbS particles distort the matrix continuity, resulting in the strength decrease. This weakening effect became more obvious when more PbS was added in the geopolymer. PbSO_4 and PbO should be placed in the same category according to their solubility under alkaline condition. However, the effects of these Pb compounds on the compressive strength of geopolymer are different. A slight loss of mechanical strength is observed when 1.5% PbSO_4 is incorporated into the geopolymeric matrix. Further increase in

Table 5

The 7 days compressive strength of the geopolymer synthesized with different lead contaminants.

ID	Contaminant in solid components/wt.%	7 days compressive strength/MPa
A	–	64.8 ± 4.2
B1	1% Pb as PbO	67.6 ± 3.8
B2	4% Pb as PbO	68.6 ± 3.3
B3	8% Pb as PbO	74.3 ± 6.4
C1	1% Pb as PbSO_4	63.9 ± 10.5
C2	4% Pb as PbSO_4	48.5 ± 6.9
C3	8% Pb as PbSO_4	31.6 ± 1.2
D1	1% Pb as PbS	53.6 ± 5.3
D2	4% Pb as PbS	50.1 ± 3.9
D3	8% Pb as PbS	46.8 ± 3.7

heavy metal dosage results in the severe strength drop. It is reasonable to infer that the difference in compressive strength caused by PbSO_4 and PbO could be due to the SO_4^{2-} . Boonserm et al. [33] studied the effects of flue gas desulfurization gypsum (FGDG) on the compressive strength of geopolymer, and found that the geopolymer strength was decreasing with the FGDG content. It was attributed to the thenardite phase, which existed as an impurity and decreased the strength. In present research, Na_2SO_4 is detected in the XRD diffractograms of sample C3. As PbSO_4 was dissolved in sodium silicate solution, it released SO_4^{2-} . When the concentration of Na_2SO_4 in the activator reached saturation, the Na_2SO_4 began to precipitate. Thus, the reason for the strength decrease in sample C seems to be similar with that found by Boonserm [33].

3.4. XPS analysis

The XPS spectra of Pb 4f of sample B3, C3 and D3 are showed in Fig. 4. There is no split peaks or shoulders in the spectra. The binding energies of Pb 4f 7/2 and Pb 4f 5/2 in sample D3 are

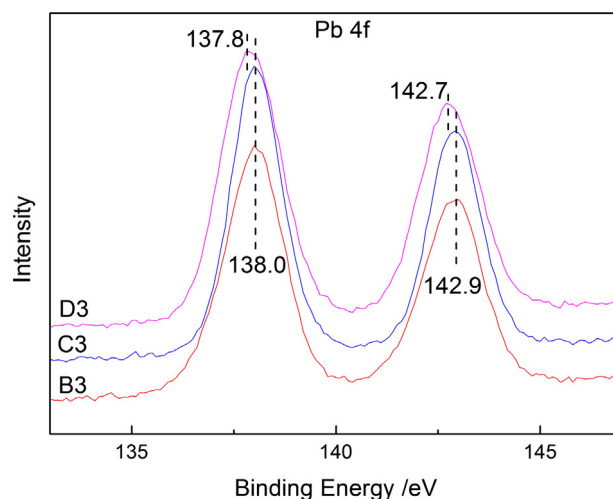


Fig. 4. The XPS spectra of Pb 4f.

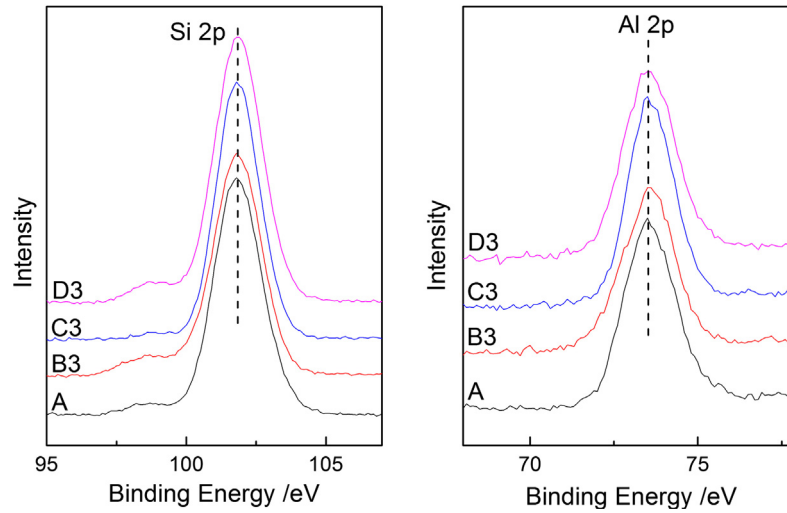


Fig. 5. The XPS spectra of Si 2p and Al 2p.

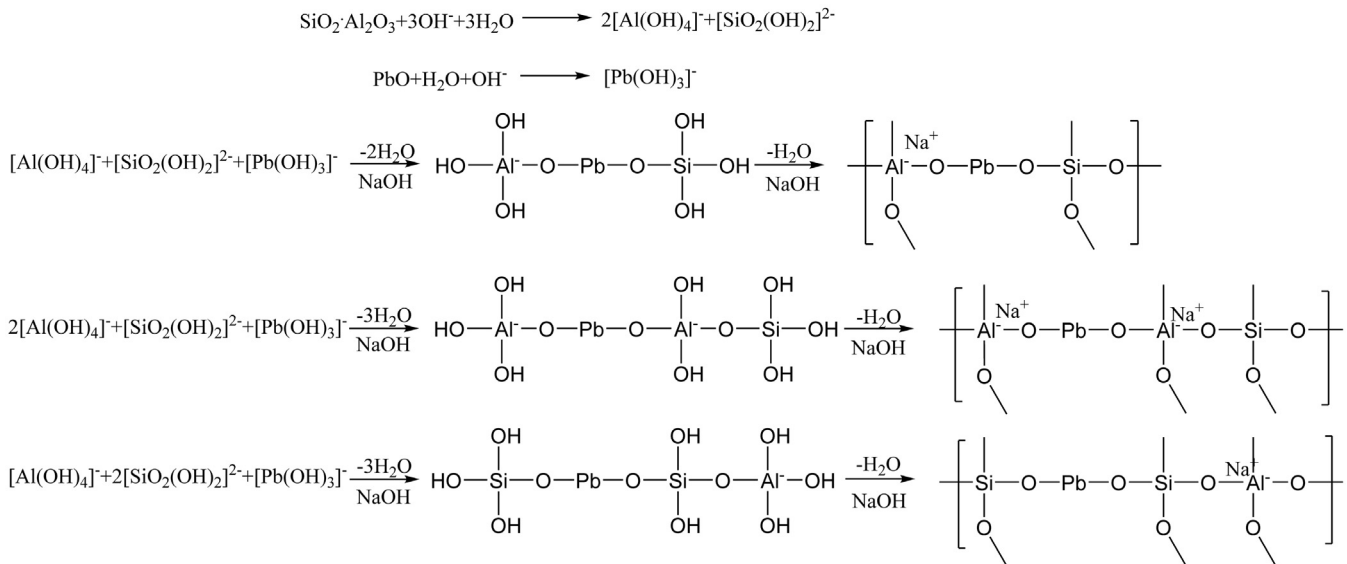


Fig. 6. The schematic formation process of leaded geopolymer.

137.8 ± 0.3 eV and 142.7 ± 0.3 eV. These values are in agreement with the values of PbS reported in the literature [34]. The binding energies of the Pb 4f in sample B3 and C3 are equal, which are higher than the binding energies of the Pb 4f in sample D3. It means the chemical environment of Pb in sample D3 is different from the environment of Pb in sample B3 and C3.

The XPS spectra of Si 2p and Al 2p of sample A, B3, C3 and D3 are showed in Fig. 5. The XPS spectra of Si 2p of sample A, B3, C3 and D3 are similar. In sample B3 and C3, the chemical environments of Si and Al seem not to be affected by Pb, although the Pb is participated in the formation of geopolymer gel. The most likely reason is that Pb is not connected with Si or Al directly. Pb is linked as Pb-O-Si or Pb-O-Al in the geopolymer structure. There are two evidences to support this hypothesis. (a) When lead compound is dissolved in alkali solutions, lead forms mononuclear or polynuclear complexes such as $[\text{Pb}(\text{OH})_3]^-$ and $[\text{Pb}_3(\text{OH})_4]^{2+}$ [35]. The speciation of Pb is more complex in high alkali solution. When soluble Na-siloxonate is dissolved in alkali solution, it also forms mononuclear or polynuclear complexes such as $\text{Si}(\text{OH})_4$ [36]. (b) the bind-

ing energies of Pb 4f 7/2 and Pb 4f 5/2 of sample B3 and C3 are 138.0 ± 0.3 eV and 142.9 ± 0.3 eV, which are equal to the values of PbO observed by Rondon et al. [37]. Thus, the schematic formation process of leaded geopolymer is showed in Fig. 6. $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ is used to represent aluminosilicate source. PbO is used to represent soluble Pb compound. It is unknown that Pb is bonded into the geopolymeric structure via Pb-O-Al, Pb-O-Si or both. Three possible formation processes are included.

3.5. Leaching test

Table 6 show the leaching results of some selected samples. The leached rate of Pb was calculated as follows,

Leached rate of the geopolymer sample

$$= \frac{C_{\text{Pb}} \times R_{L/S} \times (1 + R_{A/S})}{10^4 \times A_{\text{Pb}}} \times 100\% \quad (2)$$

$$\text{Leached rate of the raw material} = \frac{C_{\text{Pb}} \times R_{L/S}}{10^4 \times A_{\text{Pb}}} \times 100\% \quad (3)$$

Table 6

Leaching results of the geopolymer samples B3, C3 and D3 and their solid raw materials containing Pb in various chemical forms.

ID	Contaminant in solid components/wt.%	Ion concentration/mg.L ⁻¹	Leached rate/%
B3	8% Pb as PbO	26.52	1.028
B3-r	8% Pb as PbO	1992.5	49.813
C3	8% Pb as PbSO ₄	6.06	0.235
C3-r	8% Pb as PbSO ₄	115.6	2.890
D3	8% Pb as PbS	9.97	0.386
D3-r	8% Pb as PbS	174.4	4.360

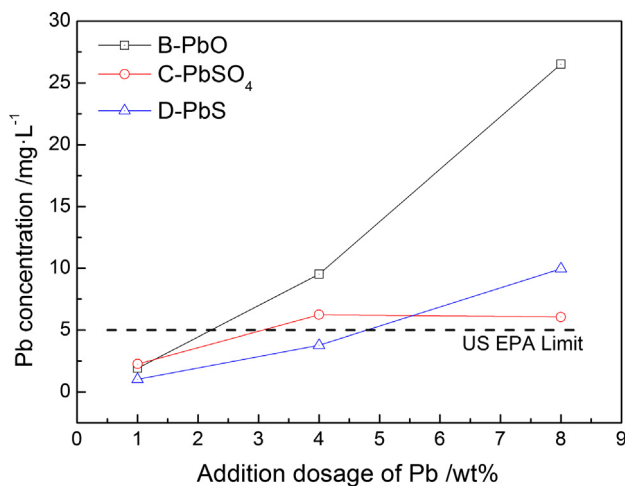


Fig. 7. The Pb concentration in the leachate of the geopolymer samples containing Pb in different chemical forms.

where C_{pb} is the Pb concentration in the leachate (mg/L); A_{pb} is the amount of Pb added into the fly ash (%); $R_{L/S}$ is the ratio of extraction fluid volume to sample weight (mL.g⁻¹); $R_{A/S}$ is the ratio of activator to solid material (g).

The concentration of Pb ions in the leaching solution of sample B3-r is higher than that of samples C3-r and D3-r. For the sample B3-r, almost half of the added Pb was dissolved in the acetic acid solution. For the sample C3-r, 2.890% of the added PbSO₄ was dissolved in the acetic acid solution. For the sample D3-r, the dissolved amount of PbS was 4.360%. The leached rates of Pb ions for the geopolymer samples B3, C3 and D3 are declined after immobilization. Geopolymeric matrices possess obvious immobilization capacity for PbO, PbSO₄ and PbS. The leached rate of Pb ions of sample B3 is 48 times lower than its raw material.

Figs. 7 and 8 show the leaching results of the geopolymer samples. With PbO and PbS addition, the concentration of Pb ions in the leaching solutions is increasing with the additional dosage. However, the other line exhibits different trends. With PbSO₄ addition, the leached Pb concentration does not rise with the increasing dosage of Pb from 4% to 8%. For all the samples, the immobilization efficiency of Pb is higher than 98.9%. It is noteworthy that the leached rate of Pb of the samples with PbSO₄ addition is decreasing as the Pb contamination increases from 1% to 8%. This is due to the inhibition of SO₄²⁻ to the leaching of Pb. The SO₄²⁻ comes from the dissolved Na₂SO₄. The detected Na₂SO₄ in sample C3 can support this interpretation.

In the case of PbS addition, PbS remains in its initial form in the geopolymer samples. PbS is immobilized in the geopolymer only by physical encapsulation. In the case of PbO and PbSO₄ addition, the Pb is converted to an amorphous form and participates in the formation of geopolymer network. The Pb is immobilized by the

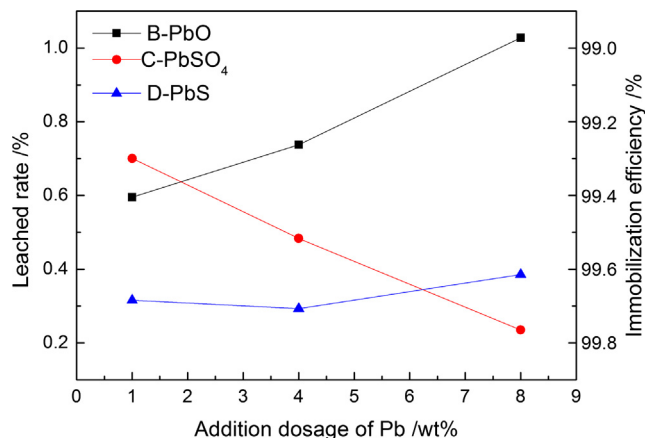


Fig. 8. Leached rate and immobilization efficiency of Pb.

Table 7

Upper limits of Pb content.

Pb compounds	Upper limit of Pb
PbO	<4%
PbSO ₄	<4%
PbS	4–8%

combined effect of physical encapsulation and chemical bonding. It is noteworthy that the leached concentration of Pb of the samples with PbO addition is higher than the samples with PbS addition. In addition, the leached rate of Pb of the samples with PbO addition is increasing as the Pb contamination increases from 1% to 8%. It means that in acetic acid medium, PbS is more stable than the Pb which is chemically immobilized in the geopolymer. The immobilization efficiency of Pb is reduced with the increasing of PbO addition. When the Pb participates in the formation of geopolymer network, the acid resistance of this structure is reduced.

Table 7 shows the upper limit of the Pb content, which can be immobilized in the geopolymer. This parameter could be regarded as the threshold value of Pb content, which could be added in geopolymer. The upper limit of the Pb content varies with the form of lead. This parameter would be used as a reference values when geopolymer technology is used for disposal of solid waste containing Pb.

4. Conclusions

The behavior of Pb ions in geopolymeric binders depends on the chemical properties of the Pb compounds. Pb can be chemically bonded into the amorphous 3D network of the geopolymeric matrix. In the case of PbO addition, Pb is dispersed throughout the geopolymeric matrix, forming leaded geopolymer. However, in case of PbS addition, PbS is segregated from the binder. Therefore, the dissolution of lead compounds is a vital reaction step in the formation of leaded geopolymer. When Pb contamination was added in the form, soluble in sodium hydroxide solution, the Pb ions will disperse throughout the geopolymeric matrices. Immobilization of these species proceeds not only by physical encapsulation, but also by chemical bonding. In contrast, the Pb compounds, inert to alkali, are trapped in the geopolymeric matrices mainly by the physical encapsulation.

Leaching data show that the Pb compounds, which are inert to the acetic acid solution, are immobilized in the geopolymer more effectively. The anions that react with Pb ions to form precipitates

can inhibit the leaching of Pb. The upper limit of the Pb content, which can be immobilized in the geopolymer, varies with the form of lead. In acetic acid medium, PbS is more stable than the Pb which is chemically immobilized in the geopolymer. It would be reasonable to believe that the form of contamination in the geopolymeric matrices is critical to the immobilization effect.

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